

SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT

Preliminary Draft Staff Report Proposed Amended Rule 1112.1 – Emissions of Particulate Matter and Carbon Monoxide from Cement Kilns

July, 2007

Deputy Executive Officer
Planning, Rule Development and Area Sources
Elaine Chang, DrPH

Assistant Deputy Executive Officer
Planning, Rule Development and Area Sources
Laki Tisopulos, Ph.D., P.E.

Senior Manager
Larry M. Bowen, P.E.

Authors: Robert R. Pease, P.E. - Program Supervisor
Henry Pourzand – Air Quality Specialist

Reviewed By: Barbara Baird - District Counsel
John Olvera- Senior Deputy District Counsel

Contributors: Tom Chico – Program Supervisor

SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT

GOVERNING BOARD

Chair: WILLIAM A. BURKE, Ed.D.
Speaker of the Assembly Appointee

Vice Chair: S. ROY WILSON, Ed.D.
Supervisor, Fourth District
Riverside County Representative

MEMBERS:

MICHAEL D. ANTONOVICH
Supervisor, Fifth District
Los Angeles County Representative

BILL CAMPBELL
Supervisor, Third District
Orange County Representative

JANE W. CARNEY
Senate Rules Committee Appointee

RONALD O. LOVERIDGE
Mayor, City of Riverside
Cities Representative, Riverside County

GARY OVITT
Supervisor, Fourth District
San Bernardino County Representative

JAN PERRY
Councilmember, 9th District
Cities Representative, Los Angeles County, Western Region

MIGUEL PULIDO
Mayor, City of Santa Ana
Cities Representative, Orange County

TONIA REYES URANGA
Councilmember, City of Long Beach
Cities Representative, Los Angeles County, Eastern Region

VACANT
Governor's Appointee

DENNIS YATES
Mayor, City of Chino
Cities Representative, San Bernardino County

EXECUTIVE OFFICER

BARRY R. WALLERSTEIN, D.Env.

TABLE OF CONTENTS

EXECUTIVE SUMMARY	1
BACKGROUND	1
Purpose.....	1
Portland Cement Manufacturing.....	5
Carbon Monoxide Formation in Cement Kilns	5
Factors Affecting Carbon Monoxide Formation.....	6
TIME AVERAGING PERIOD MODELING FOR CPCC	7
Specific Factors.....	7
Historical Data and Analysis	8
SOCIO-ECONOMIC ISSUES	8
PROPOSED AMENDMENT	9
CONCLUSION.....	9

EXECUTIVE SUMMARY

Currently, California Portland Cement Company (CPCC), is the only company in the SCAQMD that manufactures Gray Portland Cement (cement). The company is located in Colton, in San Bernardino County. Cement is used primarily as a construction material in the industrial sector due to the strength and durability of the product. It is currently being manufactured in two kilns at Colton, Kiln #1 and Kiln #2. The production process results in a variety of kiln emissions including CO and NOx. CPCC has come up with an emissions control strategy for mitigating NOx. The process involves injection of used tires into the kiln which lowers the oxygen concentration while maintaining the kiln combustion dynamics. While the process modifications at CPCC have had a beneficial impact in reducing overall CO emissions as well, it does occasionally result in increased CO formation over brief periods of time, exceeding the Rule 407 CO emissions limit of 2,000 ppm averaged over 15 consecutive minutes. The purpose of the proposed rule amendment is to acknowledge the air quality benefit by CPCC reducing NOx emissions and establish an alternative emission limit for cement kilns by extending the averaging time period for kiln CO emissions and an annual mass CO emissions limit that ensures air quality standards and local ambient air quality are not compromised. The reduction of NOx emissions is a priority since it is a precursor of both PM10 and ozone. There have been no violations of the CO standard in the AQMD since 2002 and prior to that only a small upwind portion of south Los Angeles County, far from the facility in San Bernardino County, periodically exceeded the CO standard. The region has recently been redesignated as attainment for the federal ambient CO standard by U.S. EPA. Also CO concentrations are localized near the source of emissions and do not have regional impacts as do some air contaminants. Conversely, the area surrounding CPCC is in non-attainment for both ozone and PM10. Staff proposes that Rule 1112.1 which specifically regulates cement kilns be amended to include an alternative CO standard of 2,000 ppm averaged over 3 hours and an annual mass emission reduction of CO from a 2003 baseline. Air quality modeling at CPCC indicates that ambient CO levels will not adversely affected by the alternative kiln standard.

BACKGROUND

Purpose

CPCC is currently the only facility manufacturing cement in the SCAQMD. The facility is a RECLAIM source and has undertaken a program to reduce NOx from two on-site kilns. The process involves injection of used tires into the cement kiln. A consequence of this strategy is an increase in CO emissions over very brief periods, exceeding the current Rule 407(a)(1) CO threshold which reads:

- “(a) A person shall not discharge into the atmosphere from any equipment :
 - (1) Carbon monoxide (CO) exceeding 2,000 ppm by volume measured on a dry basis, averaged over 15 consecutive minutes.”

In support of the NO_x reduction strategy CPCC has asked the District for assistance in structuring a compliance strategy for CO specific to cement kiln operations. Staff has examined an array of options including a combination of lowering the emissions threshold in conjunction with an increased averaging period. Staff is recommending amendments that will not cause or contribute to exceedences of either the one or eight hour state standards for CO and are not projected to have a significant impact on local ambient air quality. In addition the standard, compliance procedures, and test methods for CO will be more precisely defined. The reduction of NO_x is emphasized over CO as NO_x is a precursor to both ozone and PM₁₀. Figures 1 through 4 show historical ambient air quality within the SCAQMD for ozone, PM₁₀ and PM_{2.5}, respectively.

Figure 1. Number of days the 1-hour federal OZONE standard (> 0.12 ppm) was exceeded in 2005

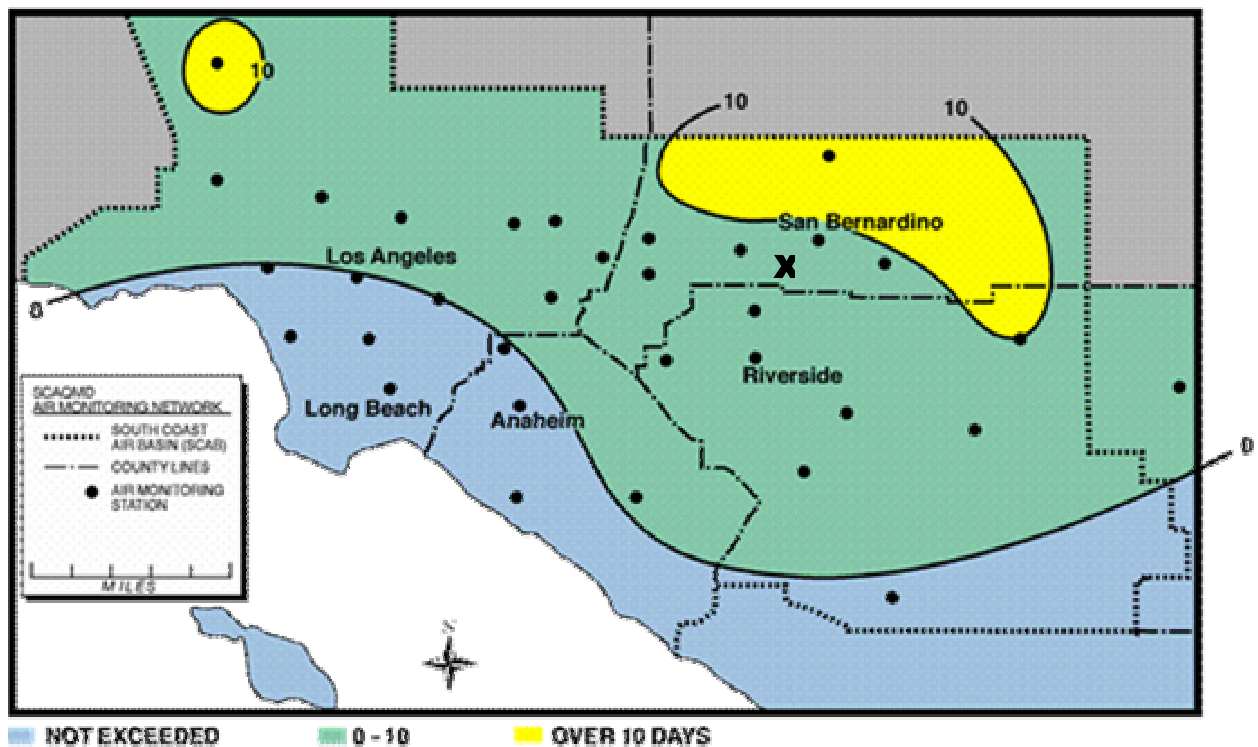


Figure 2. Number of days the 8-hour federal OZONE standard (> 0.08 ppm) was exceeded in 2005

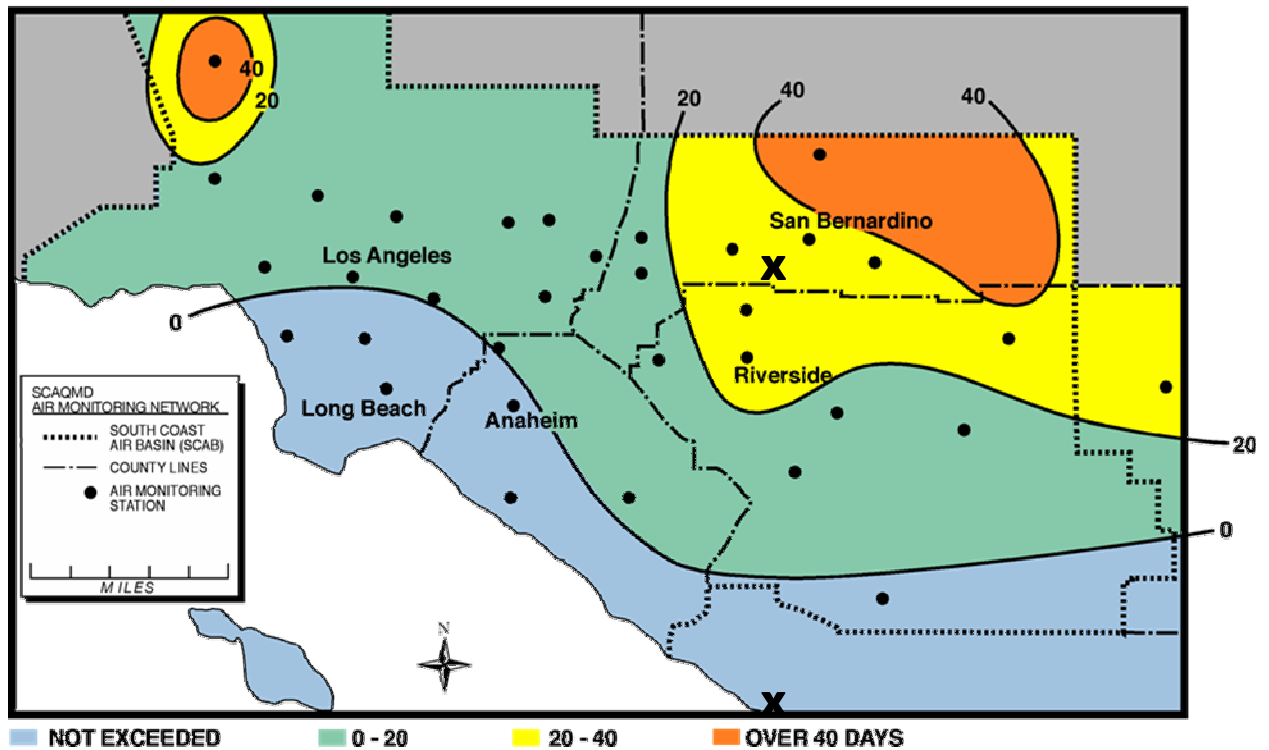


Figure 3. 2005 PM₁₀ Annual Arithmetic Mean ($\mu\text{g}/\text{m}^3$) compared to $50 \mu\text{g}/\text{m}^3$ federal standard

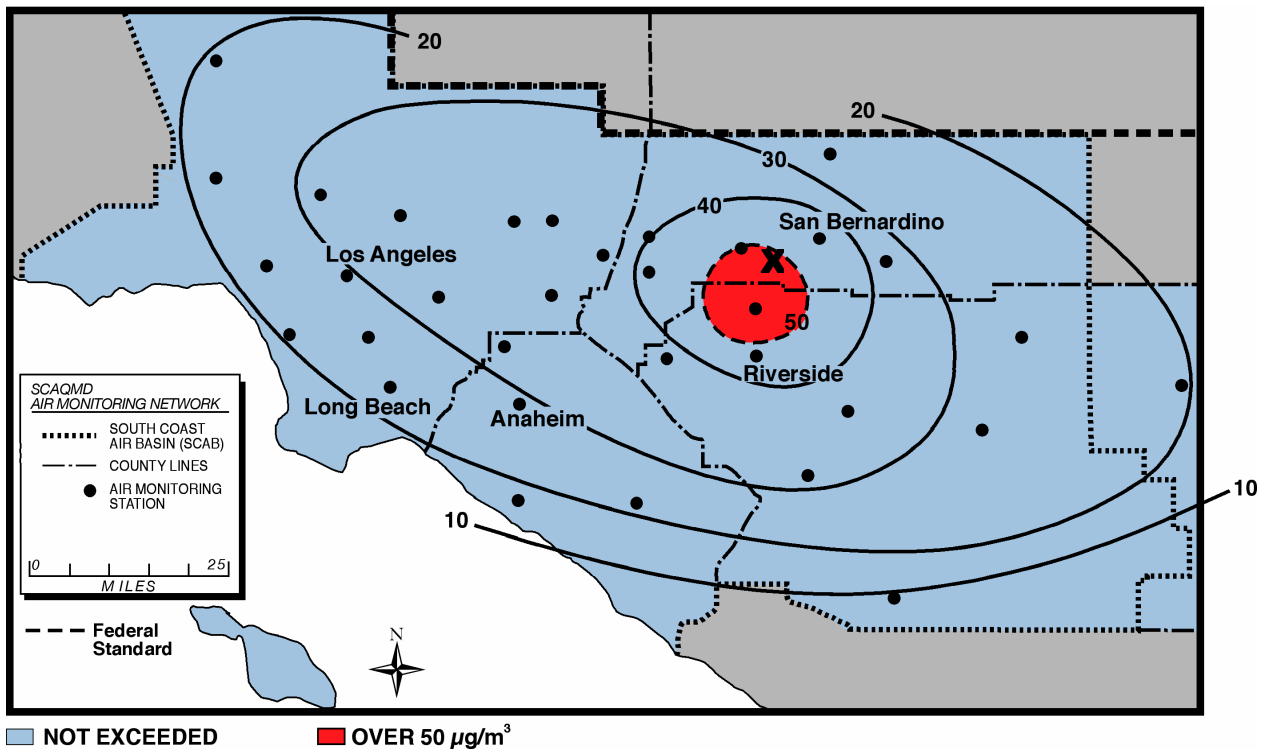
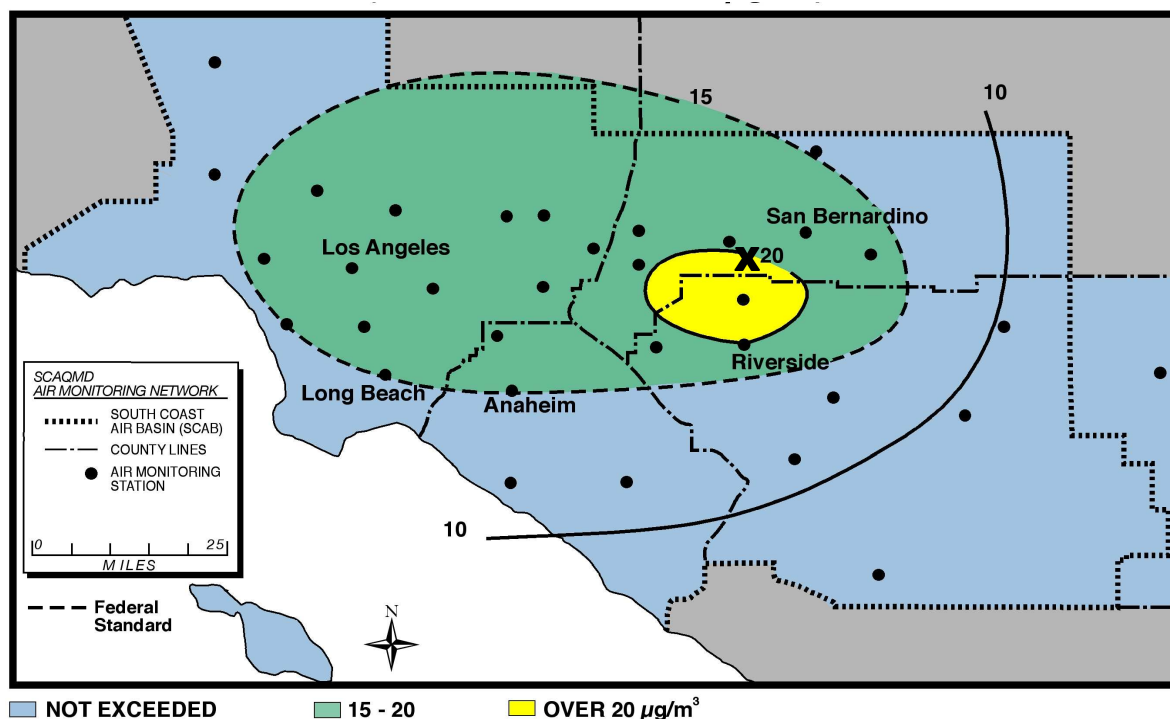


Figure 4. 2005 PM_{2.5} Annual Arithmetic Mean ($\mu\text{g}/\text{m}^3$) compared to 15 $\mu\text{g}/\text{m}^3$ federal standard



Exceedences for ozone, PM₁₀ and PM_{2.5} were recorded throughout the basin with the highest concentrations occurring in the general area where the CPCC facility is located (as indicated by the symbol **X**). In contrast, the localized exceedance of CO has historically been confined to a limited area in south Los Angeles County. In 2005, for the third consecutive year since 2003, no areas in the Basin exceeded the CO air quality standards. The Basin has been officially designated as being in attainment with federal CO standards by U.S. EPA. The highest concentrations of CO continued to be recorded in the areas of Los Angeles County where vehicular traffic is most dense with the highest concentration continuing to be south central Los Angeles county, far upwind of CPCC. The highest 8-hour average CO concentration recorded for 2005 was 5.9 ppm, in the South Central Los Angeles County area, and was 62% of the federal CO standard.

In contrast, for 2005 the Basin exceeded federal and state standards for ozone, PM₁₀ and PM_{2.5}. For ozone, the maximum 1-hour average (0.182 ppm) and maximum 8-hour average (0.145 ppm) concentrations were both recorded in the central San Bernardino Mountains area to the north-east of CPCC and were 146% and 171% of the federal standard, respectively. The Central San Bernardino Mountains area recorded the greatest number of exceedences (80 days) of both the state and federal 1-hour (18 days) and 8-hour (69 days) standards in addition to 7 days for the health advisory level (Figures 1 and 2).

For PM₁₀, the maximum annual average concentration (52 $\mu\text{g}/\text{m}^3$) occurred in the Metropolitan Riverside County area, in the general vicinity of CPCC (Figure 3). For PM_{2.5}

the maximum 24-hour average ($132.7 \mu\text{g}/\text{m}^3$) and annual average ($21.0 \mu\text{g}/\text{m}^3$) concentrations were recorded in the East San Gabriel Valley area and the Metropolitan Riverside County area, both in the general vicinity of CPCC, and were 203% and 139% of the federal standard, respectively. Figure 4 shows the 2005 PM_{2.5} Annual Arithmetic Mean concentration as compared to $15 \mu\text{g}/\text{m}^3$ federal standard.

Furthermore, about 13% (154 tons/day) of the total annual total NO_x inventory in the Basin is from stationary sources in contrast to only 1.4% (99 tons/day) from CO. The data indicates that efforts to mitigate ozone, PM₁₀ and PM_{2.5}, by controlling NO_x and particulate emissions, remain the highest priority at CPCC..

Portland Cement Manufacturing

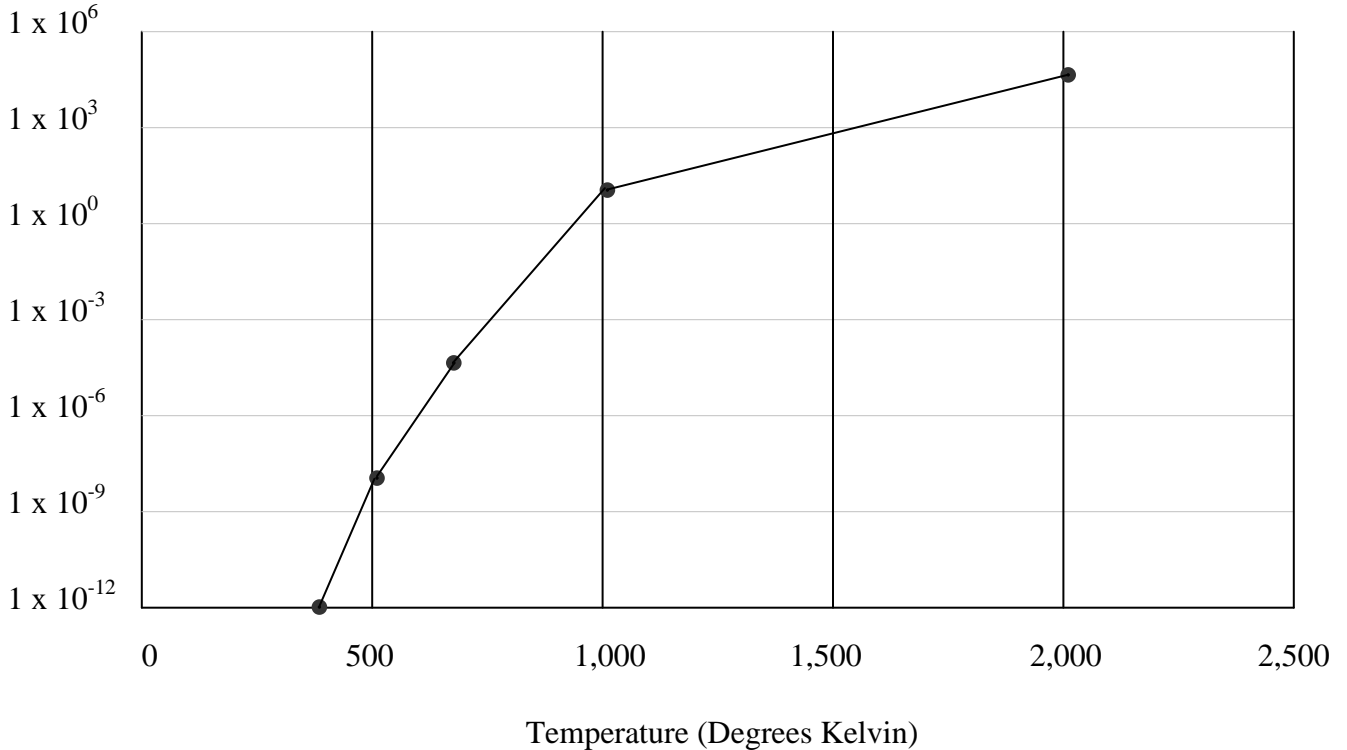
The name Portland Cement (cement) refers to a process that was patented in 1824 and is not associated with any particular location or person. The process of manufacturing cement begins with the quarrying of “Raw Mix” which is predominantly limestone rock. Raw Mix is then refined through a series of mechanical grinding and crushing operations which not only segregate but significantly reduce the diameter of the component quarried materials. The segregated materials as well as other materials brought to the facility and used in the manufacturing process are stored in silo bins. From here, limestone, shale, iron ore and silica in proprietary proportions, or kiln mix, are pneumatically feed into the feed end of each kiln. It takes approximately 1.56 parts of this kiln feed to manufacture 1 part of Portland cement. Each kiln is basically a huge rotating cylinder lined with refractory fire brick that is several hundred feet long. A slight incline from the horizontal causes the spinning material in the kiln to travel down the length of the kiln from the feed end to the discharge end. A large burner located at the discharge end of the kiln fires the transitory kiln feed. Reaction zones are established towards the center and in towards the horizontal axis of the kiln as the feed mix is oxidized and the resulting reactions produce an intermediate product called clinker that is collected at the discharge end. Clinker is a harder material than any of the quarried rock that comprises the feed mix. In the final phase, the clinker is milled and packaged with gypsum to produce cement. Cement when mixed in the correct proportion with water sets to form concrete.

Carbon Monoxide Formation in Cement Kilns

Quarried limestone is not a homogenous material but is composed mostly of limestone which is also the principle ingredient for manufacturing cement. Limestone is predominantly Calcium Carbonate (CaCO_3). The production of cement involves chemical reactions in which the feed mix in the kiln is heated to high temperatures and oxidation of the feed mix occurs. The oxidation of carbon compounds results in the formation of carbon monoxide (CO) and carbon dioxide (CO_2). Both are present to an extent in the kiln during clinker production. In the kiln, two factors influence the proportions of CO to CO_2 . First, the amount of oxygen present and second, the temperature in the reaction zone of the kiln. In general, the more oxygen available the more carbon monoxide is reduced to carbon dioxide. Figure 8 shows that higher kiln temperatures tend to increase the oxidation of CO to CO_2 .

Figure 8. Increasing Rate Constant for Oxidation of CO with Temperature

Rate Constant (c.c. per mol)



Factors Effecting Carbon Monoxide Formation

The production of cement also results in oxides of nitrogen (NOx) emissions. NOx emissions from kiln reactions are a byproduct of using air to feed the kiln, the fuel used, and the nature of the combustion process. Both NOx and CO result from the chemistry and temperature environment that occurs in the kiln process. The problem is that conditions favoring mitigation of NOx, namely limiting the presence of air and reducing peak combustion temperatures lead to increased CO emissions. Paradoxically, the converse also holds and the presence of excess air (or oxygen) and higher kiln temperatures increases the proportion of kiln NOx emissions. The tire injection NOx control strategy developed specifically for CPCC minimizes the presence of air while maintaining kiln temperatures by providing a packet of energy when the tire is burned in the kiln in an exothermic reaction. CO spiking can be mitigated with this approach. There are also practical limitations on the amount of excess air that could be introduced into the kiln process to address CO emissions. Too much air would be inefficient both in terms of the extra energy needed to drive the increased volume flow through the kiln and also because of the increased fuel needed to maintain optimal kiln temperatures.

TIME AVERAGING PERIOD MODELING FOR CPCC

Specific Factors

Both Kiln #1 and Kiln #2 are analogous to extremely immense crucibles where a myriad of chemical reactions are continuously taking place. In addition, because of the design and enormous dimensions of each kiln, different reactions are taking place at the same time in different areas or zones of the kiln. Kiln feed composition and temperature can vary unpredictably within the kilns. Temperature while tending to increase towards the core of the kiln does so in a non-uniform manner. The variability in kiln feed mix composition and temperatures necessitate continuous oversight. Because of the proportions of each kiln, much can happen in the formation process of Clinker from the time feed mix enters the kiln at the feed end till it exits the kiln at the discharge end as Clinker.

A kiln operator monitors the kiln processes in real time from a remote location and makes adjustments to burner flame temperature and the other reaction variables as necessary. Even though the process is monitored in real time, the effect of any operator action can take up to twenty minutes to take place in the kiln. Variations in temperature and kiln feed mix composition sometimes lead to the formation of both “dams” and “fronts”. A dam is formed when molten feed mix cools enough to solidify, creating a dam like barrier behind which molten feed mix accumulates. In order to re-establish the flow of kiln feed material towards the discharge end of the kiln the operator must generally increase temperatures in the kiln. Even measured corrections deviate from anticipated outcomes because of the size, complexity and uncertainty of kiln operations. Eliminating a dam by increasing kiln temperatures may release an accumulation of liquefied feed mix from behind the dam. This can rush towards the discharge end creating a front or wave. A front results in the reacting kiln mixture moving faster than the desired residency time for an optimal reaction. Waves and fronts are a major concern in stabilizing kiln reactions. The experienced operators job is more anticipating how the kiln will be reacting some time in the future, in real time, and working to maintain optimal kiln conditions. In empirical observations made during site visits to CPCC and in discussions with operational and management staff the following factors were found to affect CO emissions from kilns:

1. The non-homogenous chemical composition of raw mix and hence the feed mix,
2. The varying temperatures in various reaction zones within the kilns,
3. The heterogeneous chemical composition of tires used in the injection system, and
4. The uncertain distribution of reaction zones within the kilns leading to the formation of “dams” and “fronts”.

While each kiln normally operates within a known range of settings, uncertainty about the above factors results in uncertainty about CO emissions.

Historical Data and Analysis

Raw data provided by CPCC is in the form of time averaged data from continuous emissions monitors operating on both Kiln #1 and Kiln #2, in excel file format (the CO monitors operated by CPCC have not been certified by the SCAQMD). Over two years of representative data, from 2005 through to early 2007, was used for modeling of kiln CO emissions. Since the data is in the form of actual real time observations of both kilns under operating parameters, the observations were modeled using various rolling average time periods. Each rolling average time period was representative of a target time averaging period for CO emissions concentrations measured in ppm corrected to 3% O₂, on a dry basis. Data and the resultant analysis provided by CPCC indicates that CPCC will most likely not exceed the 2,000 ppm CO emissions threshold corrected to 3% O₂ with a proposed revised time averaging period of 3 hours. The data and resultant time emissions period is summarized in the following table:

Table 1. Data and Resultant Time Averaging Period for Kiln Observations

Statistic	Kiln #1	Kiln #2
Observations/Data Points	17,985	17,986
Observation period	1/1/2005 – 2/1/2007	1/1/2005 – 2/1/2007
Maximum observation (ppm CO)	2,291	2,354
Proposed time averaging period (hours)*	3	3

*averaged CO concentration not to exceed 2,000 ppm, corrected to 3% O₂, on a dry basis

Data provided by CPCC also shows a general decrease in mass CO emissions for the past four years as shown below:

Table 2. Annual Mass Emissions (tons/year)

Year	Kiln #1	Kiln #1 Reduction**	Kiln #2	Kiln #2 Reduction**
2003	5,114	-	4,226	-
2004	3,126	39%	3,037	28%
2005	1,100	79%	1,132	73%
2006	1,005	80%	1,269	73%

**the % reduction in kiln emissions from the base year in 2003 (rounded to nearest 1%)

Based on the above trend and continued future mandatory NO_x reductions, staff also recommends that the annual combined total of all CO emissions from both kilns be limited to no more than 50% per calendar year of the combined total 2003 baseline CO emissions from both kilns.

SOCIO-ECONOMIC ISSUES

CPCC will not be required to implement any operational changes at their Colton facility. As such the proposed amendment will have no anticipated socio-economic impacts.

PROPOSED AMENDMENT

Staff is recommending that Rule 1112.1 be amended to include CO limits as well as the current particulate limits. For CO two alternatives are offered; comply with the current limit of Rule 407(a)(1) or as an alternative comply with a new proposed standard of 2,000 ppm concentration limit averaged over 3 hours plus annual CO emissions from a kiln cannot exceed 50% of the baseline 2003 CO emission.

Proposed amendments also include text on updating compliance procedures and test methods to conform with the certification requirements of Rule 218.

CONCLUSION

This study has used large amounts of data and various methods of analysis in order to estimate a time period during which the average CO kiln emissions will be unlikely to ever exceed specific threshold values corrected to 3% oxygen concentration on a dry volume basis. Analysis of historical data indicates that most exceedences are short in duration. No more than 30 minutes is usually required to average 2,000 ppm or less, however there are rare excursions as above 2,300 ppm. Since the averaging period needed to remain in compliance has generally dropped with time, some of the longer compliance averaging periods required, especially in earlier years could be attributed to breakdowns, repair and testing, equipment replacement and/or new operator inexperience as potential reasons. Data and analysis of almost 18,000 data points indicates that CO compliance can be achieved with a time averaging period of 3 hours at 2,000 ppm, corrected to 3% O₂, on a dry basis. Ambient air quality monitoring indicates no negative localized impacts. The alternative CO standard will ensure that the more problematic NO_x and PM₁₀ emissions will continue to be mitigated.